REB, The Book
Example 12.4.1 Solution

A 350 L adiabatic CSTR and a 350 L adiabatic PFR are going to be connected in series and used to convert reagent A according to irreversible reactions (1) and (2), where D is the desired product and U is an undesired, low-value byproduct. The feed consists of an aqueous stream containing 2.5 mol A L^{-1}, flowing at a rate of 100 L min^{-1} at 38 °C. The liquid density may be assumed to be constant. The heat of reaction (1) is -21,500 cal mol^{-1} and that of reaction (2) is -24,000 cal mol^{-1}. The heat capacity of the solution is constant and equal to 1.0 cal cm^{-3} K^{-1}. The rate expressions for reactions (1) and (2) are given in equations (3), and (4), respectively. The pre-exponential factor for reaction (3) is 1.2 x 10^5 min^{-1}, and the activation energy is 9100 cal mol^{-1}. The Arrhenius parameters for reaction (4) are 2.17 x 10^7 L mol^{-1} min^{-1} and 13,400 cal mol^{-1}. Compare the overall conversion of A and selectivity (mol D per mol U) for the configuration with the CSTR first to those for the configuration with the PFR first.

$$A \rightarrow D \tag{1}$$

$$A \rightarrow U \tag{2}$$

$$r_1 = k_1 C_A \tag{3}$$

$$r_2 = k_2 C_A^2 \tag{4}$$

Assignment Summary

The information provided in the assignment narrative is summarized below. The assignment does not mention pressure drop, and it doesn't provide sufficient information to write a momentum balance for the PFR, so pressure drop is assumed to be negligible.

<u>Reactions</u>

$$A \rightarrow D \tag{1}$$

$$A \rightarrow U \tag{2}$$

Rate Expressions

$$r_1 = k_1 C_A \tag{3}$$

$$r_2 = k_2 C_A^2 \tag{4}$$

Reactors: Steady-state, liquid-phase, adiabatic CSTR and steady-state, liquid-phase, adiabatic PFR with negligible pressure drop.

Given Constants: V_{CSTR} = 350 L, V_{PFR} = 350 L, $C_{A,feed}$ = 2.5 mol L^{-1}, $\dot{V}_{feed}$ = 100 L min^{-1}, T_{feed} = 38 °C, ΔH_1 = –21,500 cal mol^{-1}, ΔH_2 = –24,000 cal mol^{-1}, $\breve{C}_p$= 1.0 cal cm^{-3} K^{-1}, $k_{0,1}$ = 1.2 x 10^5 min^{-1}, E_1 = 9100 cal mol^{-1}, $k_{0,2}$ = 2.17 x 10^7 L mol^{-1} min^{-1}, E_2 = 13400 cal mol^{-1}.

Deliverables: f_A and $S_{D/U}$ for (a) the CSTR followed by the PFR, and (b) the PFR followed by the CSTR

CSTR Model Function

The purpose of the CSTR model function is to solve the CSTR design equations for the reactor. This is done numerically by calling an ATE solver. Any quantities that are not given or computable, and are required for solving the design equations will be passed to it as arguments. If the CSTR residuals function requires any quantities that cannot be passed to it as arguments, the CSTR model function will make them available to it as global variables. The CSTR residuals function described here also must be written.

CSTR Model Equations:

$$0 = \dot{n}_{A,in} - \dot{n}_{A,out} + \left(-r_1 - r_2\right) V_{CSTR} = \epsilon_1 \tag{5}$$

$$0 = \dot{n}_{D,in} - \dot{n}_{D,out} + r_1 V_{CSTR} = \epsilon_2 \tag{6}$$

$$0 = \dot{n}_{U,in} - \dot{n}_{U,out} + r_2 V_{CSTR} = \epsilon_3 \tag{7}$$

$$0 = -\dot{V}_{in} \check{C}_p \left(T_{out} - T_{in}\right) - V_{CSTR} \left(r_1 \Delta H_1 + r_2 \Delta H_2\right) = \epsilon_4 \tag{8}$$

CSTR Model Variables: $\dot{n}_{A,out}$, $\dot{n}_{D,out}$, $\dot{n}_{U,out}$, T_{out}

Additional Computable Unknowns: r_1, r_2, k_1, k_2, C_A, and $\dot{V}_{out}$

$$k_i = k_{0,i} \exp\left(\frac{-E_i}{R T_{out}}\right) \quad i = 1 \text{ and } 2 \tag{9}$$

$$C_A = \frac{\dot{n}_{A,out}}{\dot{V}_{out}} \tag{10}$$

$$\dot{V}_{out} = \dot{V}_{feed} \tag{11}$$

Additional Uncomputable Unknowns: $\dot{n}_{A,in}$, $\dot{n}_{D,in}$, $\dot{n}_{U,in}$, and T_{in}

ATE Solver Inputs:

1. Initial guesses for the reactor model variables

$$\dot{n}_{i,out,guess} = \dot{n}_{i,in} \quad i = A, D, \text{ and } U \tag{12}$$

$$T_{out,guess} = T_{in} + 10\ \text{K} \tag{13}$$

2. Residuals function that
   a. receives guesses for the CSTR model variables
   b. has access to $\dot{n}_{A,in}$, $\dot{n}_{D,in}$, $\dot{n}_{U,in}$, T_{in}
   c. calculates the additional unknowns using equations (3), (4), and (9) - (11)
   d. evaluates and returns the CSTR residuals using equations (5) - (8)

PFR Model Function

The purpose of the PFR model function is to solve the PFR design equations for the reactor. This is done numerically by calling an IVODE solver. Any quantities that are not given or computable and are required for solving the design equations will be passed to it as arguments. If the PFR derivatives function requires any quantities that cannot be passed to it as arguments, the PFR model function will make them available to it as global variables. The PFR derivatives function described here also must be written.

PFR Model Equations:

$$\frac{d\dot{n}_A}{dV} = -r_1 - r_2 \tag{14}$$

$$\frac{d\dot{n}_D}{dV} = r_1 \tag{15}$$

$$\frac{d\dot{n}_U}{dV} = r_2 \tag{16}$$

$$\frac{dT}{dV} = -\frac{r_1\Delta H_1 + r_2\Delta H_2}{\dot{V}_{feed}\breve{C}_p} \tag{17}$$

PFR Model Variables: $\underline{V}$, $\underline{\dot{n}}_A$, $\underline{\dot{n}}_D$, $\underline{\dot{n}}_U$, and $\underline{T}$

Additional Computable Unknowns:

$$C_A = \frac{\dot{n}_A}{\dot{V}_{feed}} \tag{18}$$

Additional Uncomputable Unknowns: $\dot{n}_{A,in}$, $\dot{n}_{D,in}$, $\dot{n}_{U,in}$, T_{in}

IVODE Solver Inputs:

1. Initial values of the reactor model variables

$$V_{initial} = 0 \tag{19}$$

$$\dot{n}_{i,initial} = \dot{n}_{i,in} \quad i = A, D, \text{ and } U \tag{20}$$

$$T_{initial} = T_{in} \tag{21}$$

2. Stopping criterion

$$V = V_{PFR} \tag{22}$$

3. Derivatives function that
   a. receives the PFR model variables at the start of an integration step
   b. calculates the additional unknowns using equations (3), (4), (9), and (18)
   c. evaluates and returns the PFR model derivatives using equations (14) - (17)

Deliverables Function

The purpose of the deliverables function is to use the CSTR and PFR model functions above to calculate the quantities and generate the graphs necessary to fulfill the requests in the assignment narrative.

Deliverables Function

1. Solve the CSTR design equations using the process feed
2. Solve the PFR design equations using the outlet from the CSTR as the inlet
3. Calculate the conversion and final selectivity

$$f_A = \frac{\dot{n}_{A,feed} - \underline{\dot{n}}_{A,PFR}\Big|_{V=V_{PFR}}}{\dot{n}_{A,feed}} \tag{23}$$

$$S_{D/U} = \frac{\underline{\dot{n}}_{D,PFR}}{\underline{\dot{n}}_{U,PFR}}\Bigg|_{V=V_{PFR}} \tag{24}$$

4. Solve the PFR design equations using the process feed
5. Solve the CSTR design equations using the outlet from the PFR as the inlet
6. Calculate the conversion and final selectivity

$$f_A = \frac{\dot{n}_{A,feed} - \dot{n}_{A,out,CSTR}}{\dot{n}_{A,feed}} \tag{25}$$

$$S_{D/U} = \frac{\dot{n}_{D,out,CSTR}}{\dot{n}_{U,out,CSTR}} \tag{26}$$

Implementation of the Calculations

The Python script, example_12_4_1.py, that was written to perform the calculations accompanies this solution. It is structured as follows.

1. Import necessary libraries.
2. Make the given constants available wherever they are needed.
3. Declare global variables for quantities that cannot be passed to the CSTR residuals function as arguments.
4. Define the CSTR model, CSTR residuals, PFR model, PFR derivatives, and deliverables functions as described above.
5. Call the deliverables function.

Results and Discussion

The calculations were performed as described above. When the CSTR is the first reactor, the conversion is 75%, the selectivity is 2.63 moles of D per mole of U, and the final temperature is 79.6 °C. If the PFR is first, the conversion is 65.7%, the selectivity is 2.76 moles of D per mole of U and the final temperature is 74.4 °C. This trade-off might have been expected on the basis of some qualitative reasoning.

The reactions are exothermic with typical kinetics, so a large rate, and correspondingly high conversion, is favored by high temperature and high reactant concentration. The reactions occur in parallel, and the instantaneous selectivity, $S_{D/U}$, is the ratio of the desired to undesired reaction rates, as given in equation (27). Examination of that equation shows that high selectivity also is favored by high temperature (because $E_2 - E_1$ is a positive number), but by low reactant concentration (due to the $\frac{1}{C_A}$ term).

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_{0,1} \exp\left(\frac{-E_1}{RT_1}\right) C_A}{k_{0,2} \exp\left(\frac{-E_2}{RT_1}\right) C_A^2} = \frac{k_{0,1}}{k_{0,2}} \exp\left(\frac{E_2 - E_1}{RT}\right) \frac{1}{C_A} \qquad (27)$$

The temperature and the composition within the reactors are coupled through the reactor design equations. It isn't possible to change one without affecting the other. When the type of the first reactor is changed, that affects the temperature and composition in both reactors. As such, it isn't surprising that there is a trade-off between conversion and selectivity.

Deliverables

The conversion and selectivity for the two reactor configurations are shown in Table 1.

Table 1. Effect of Reactor Sequencing on Network Performance.

Reactor Sequence	Conversion (%)	Selectivity (D per U)	Outlet Temperature (°C)
CSTR then PFR	75.0	2.63	79.6
PFR then CSTR	65.7	2.76	74.4